



Microstructure of Matrix in UHTC Composites

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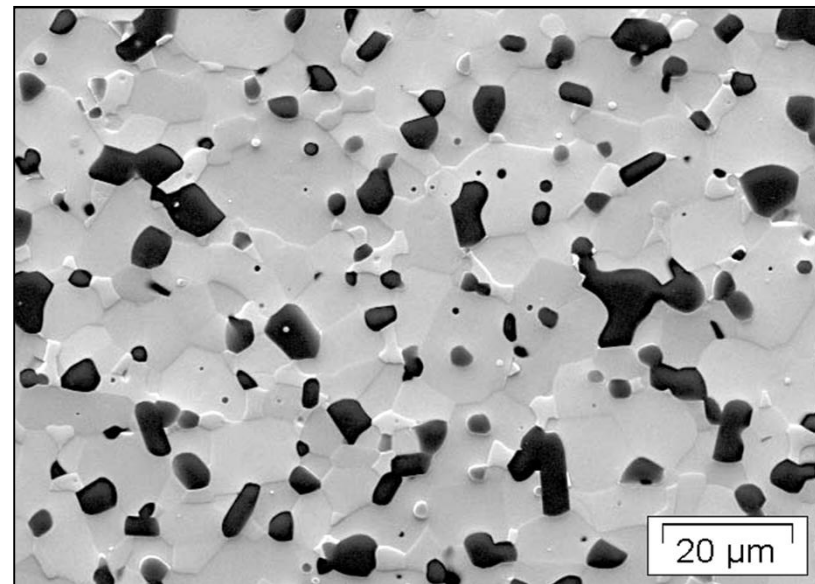
Outline

- Issues with UHTCS
- Approaches to improve fracture toughness
 - In -situ reinforcement
 - Preceramic polymer route
 - “Coating” route
 - Fiber reinforcement
 - 2D weaves
 - 3D weaves



Ultra High Temperature Ceramics (UHTCs) : A Family of Materials

- Borides, carbides and nitrides of transition elements such as hafnium, zirconium, tantalum and titanium.
- Some of highest known melting points
- High hardness, good wear resistance, good mechanical strength
- Good chemical and thermal stability under certain conditions
- High thermal conductivity (diborides).
 - good thermal shock resistance



Typical microstructure of a "monolithic" HfB₂/SiC material



Where are we going?

- What does a UHTC need to do?
 - Carry engineering load at RT
 - Carry load at high use temperature
 - Respond to thermally generated stresses (coatings)
 - Survive thermochemical environment
- High Melting Temperature is a major criterion, but not the only one
 - Melting temperature of oxide phases formed
 - Potential eutectic formation
- Thermal Stress – $R' = \sigma k / (\alpha E)$
 - Increasing strength helps, but only to certain extent
- Applications are not just function of temperature
- **Materials needs for long flight time reusable vehicles are different to those for expendable weapons systems**



UHTC Challenges: What will make designers use these materials?

- 1. Fracture toughness: Composite approach is required**
 - Integrate understanding gained from monolithic materials
 - Need high temperature fibers
 - Need processing methods/coatings
- 2. Oxidation resistance in reentry environments**

reduce/replace SiC
- 3. Modeling is critical to shorten development time, improve properties and reduce testing**
- 4. Joining/integration into a system**
- 5. Test in relevant environment—test data!**



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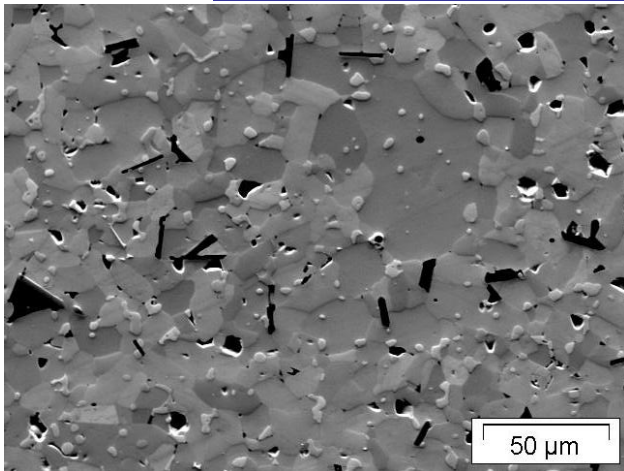


Preceramic Polymers Can Control Grain Shape

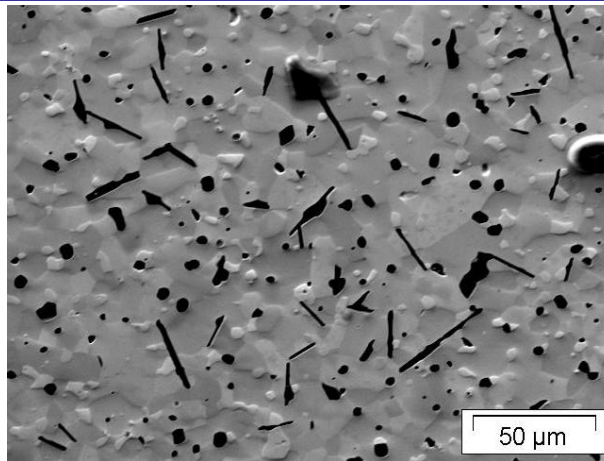
- Conventional source of SiC is powder.
- SiC from a preceramic polymer source:
 - Will affect densification and morphology.
 - May achieve better distribution of SiC source through HfB_2 .
 - Previous work shows that preceramic polymers can enhance growth of acicular particles (for fracture toughness).
- Potential to improve mechanical properties with reduced amount of SiC and also potentially improve oxidation behavior.



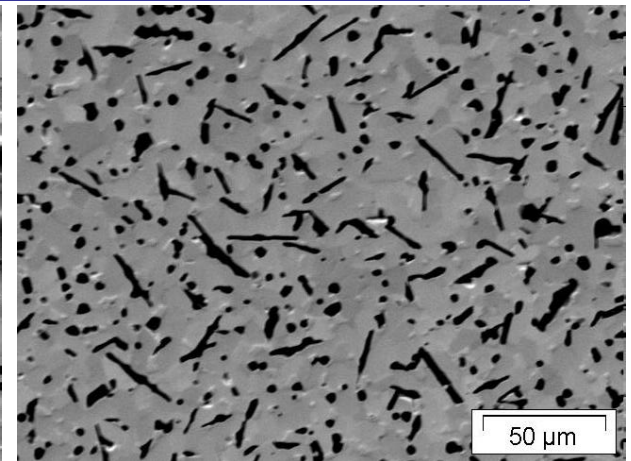
Growth of Elongated SiC Grains



5%* SiC



10%* SiC — Rod diameter $\sim 2\mu\text{m}$



15%* SiC — Rod diameter $\sim 5\mu\text{m}$

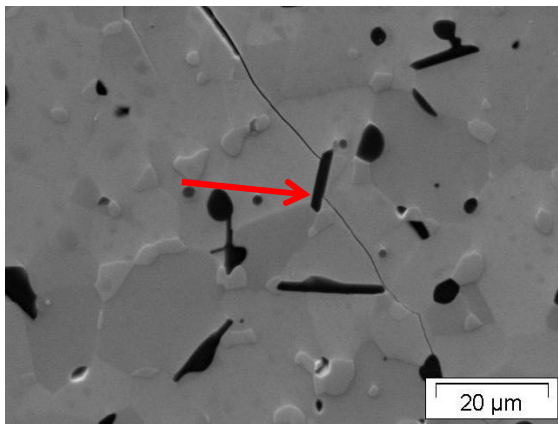
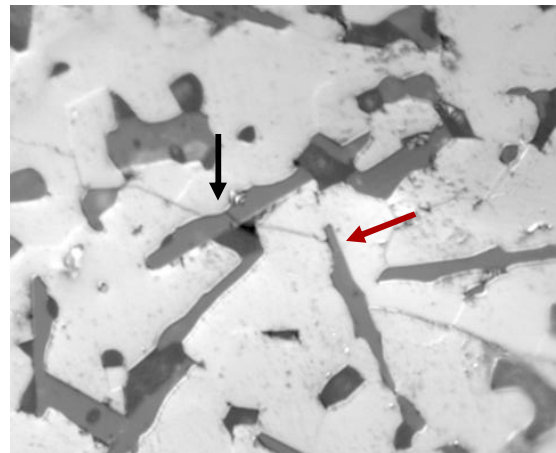
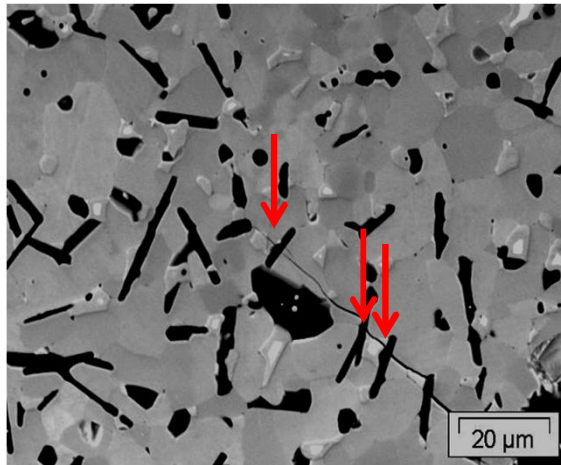
SiC Preceramic Polymer Promotes Growth of Acicular Grains

- Samples processed with 5 to >20 volume % SiC
- Can adjust volume of SiC in the UHTC without losing the high I/d architecture
- Amount of SiC affects number and thickness (but not length) of rods — length constant ($\sim 20\text{--}30\mu\text{m}$)
- Possible to obtain dense samples with high-aspect-ratio phase
- Hardness of high-aspect-ratio materials comparable to baseline material

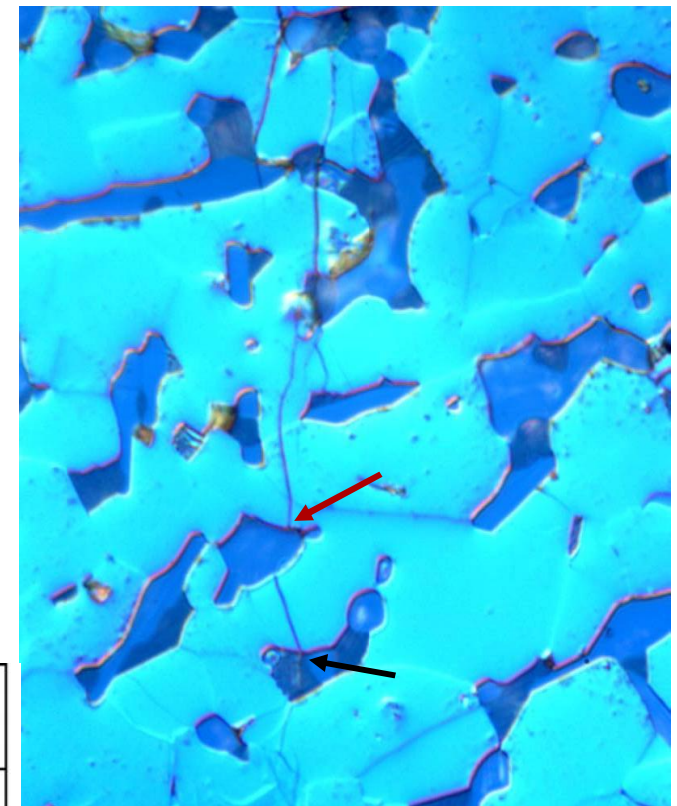
* Precursor added in amounts sufficient to yield nominal amounts of SiC



In Situ Composite for Improved Fracture Toughness



SiC Content	Fracture Toughness (MPam ^{1/2})
5%	3.61
10%	4.06
15%	4.47
Baseline UHTC (20%)	4.33



Oak Ridge National Laboratory

Evidence of crack growth along HfB₂-SiC interface, with possible SiC grain bridging

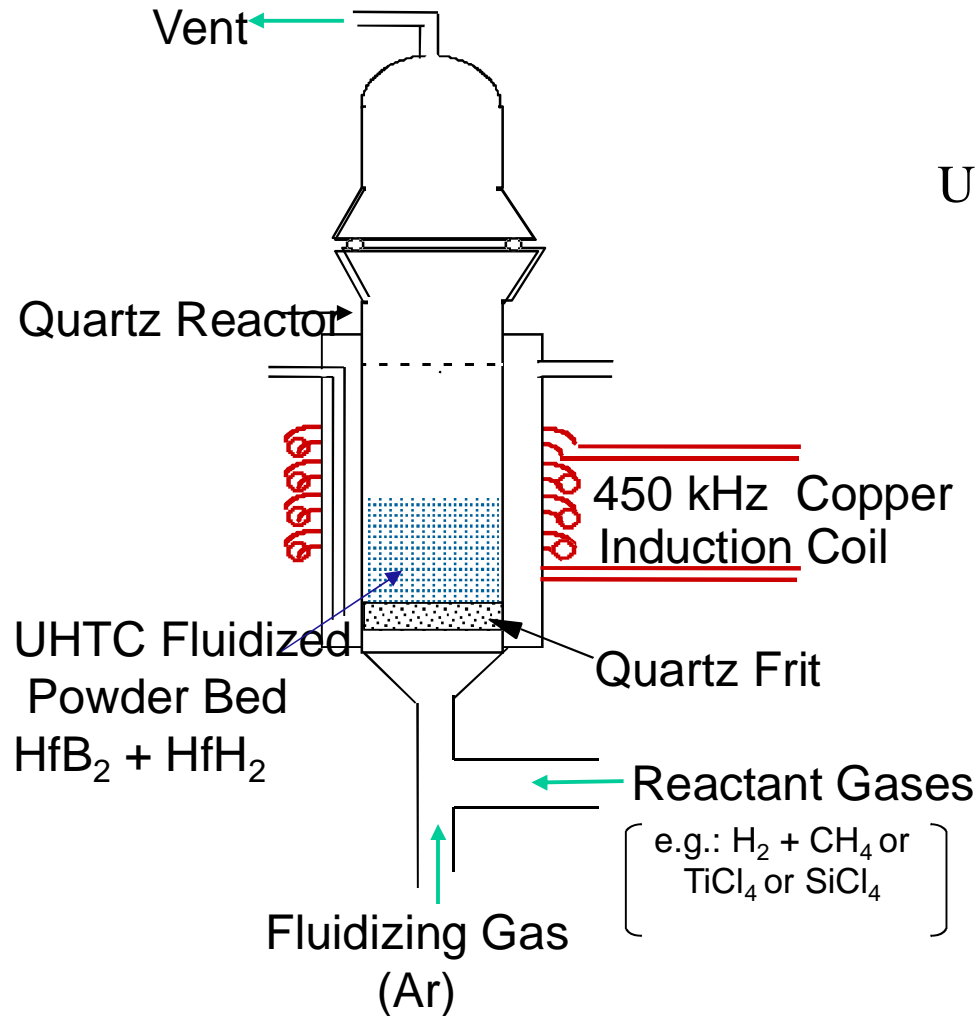


When Additives for UHTCs Are Added as Coatings

Fluidized Bed Reactor - Chemical Vapor Deposition Technique (FBR-CVD)

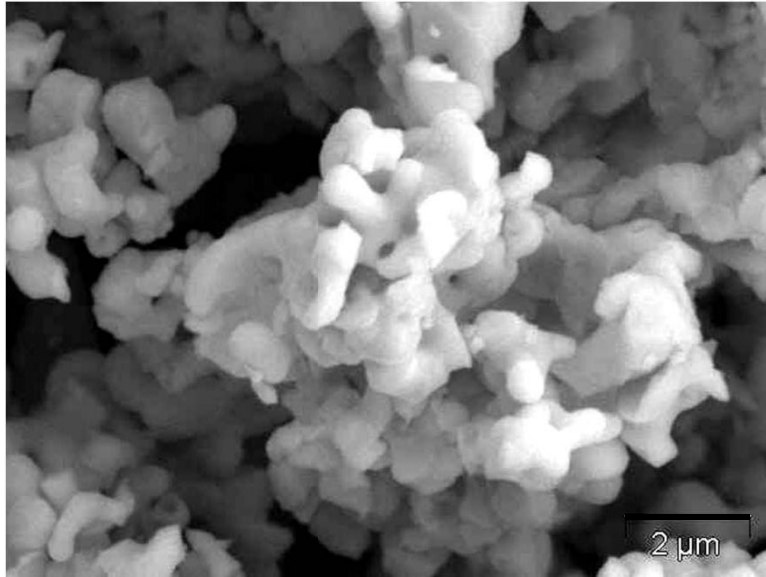
Using coatings, instead of particles, to introduce additives, offers several advantages:

- Uniform distribution and control of coating composition
- Bypasses traditional sources of processing contamination
- May lead to improved oxidation and creep resistance (less O_2 contamination)
- Amount of additive can be controlled
- Reductions in hot-press temperature, pressure, and time

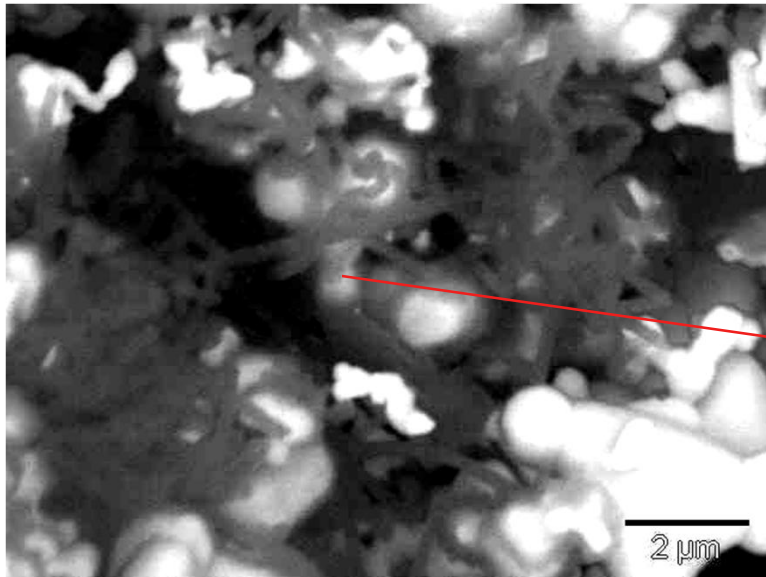




SiC Coating Appearance on Powders



Uncoated Powder

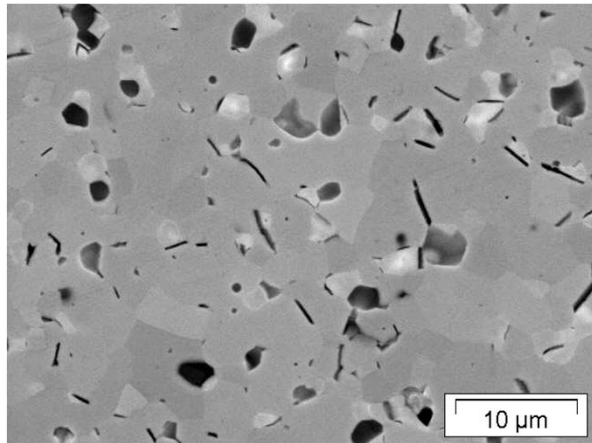
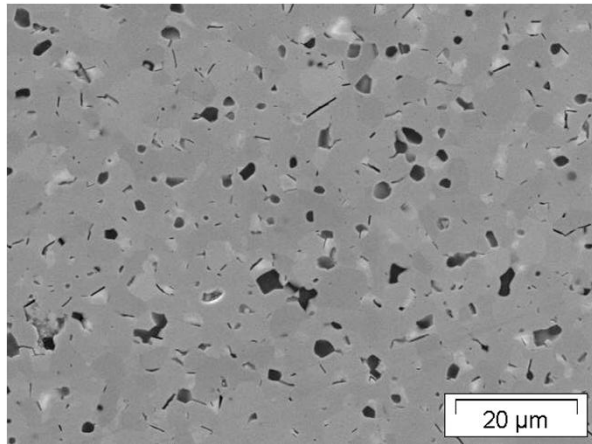


SiC Coated Powder

Gray filamentous material is SiC



Addition of SiC as “Coating”



- Alternative route to growing acicular grains
- HfB₂ powders “coated” with Si/C in fluidized bed
- Spark plasma sintered
 - Not fully dense
 - Growth of acicular SiC grains
- Grain boundaries should be very clean, leading to potential improvements in thermal conductivity

HfB₂- 5 vol-%SiC (SPS)



Processing of Composites

Objectives:

- Can we use knowledge gained from controlling microstructures in “monolithic” UHTCs to make matrices for fiber reinforced composites?
- Can both 2D and 3D weaves be infiltrated?
- Caveats
 - Using available carbon fiber structures
 - No fiber coating



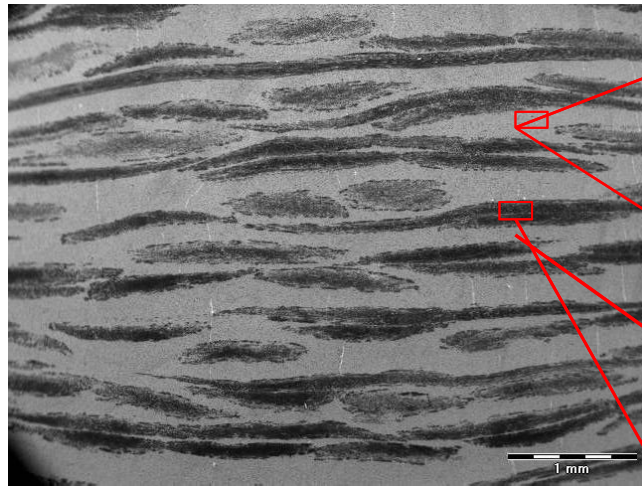
Processing of 2D Weave

Composites from 2D weaves

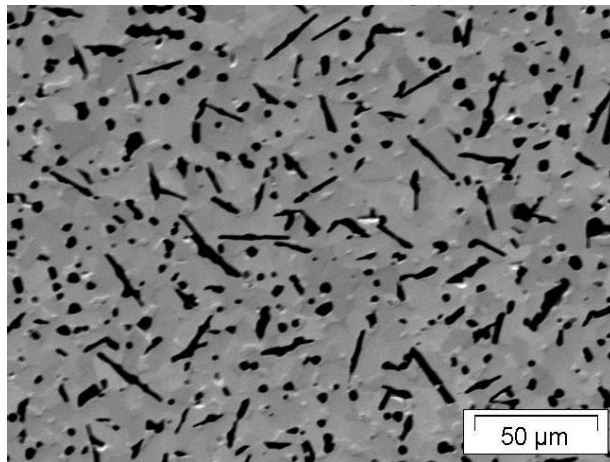
- Carbon fiber cloth (PAN-based)
- Impregnated with preceramic polymer/HfB₂ powder mixture—one infiltration per layer
- Layers stacked and hot pressed (~15 layers)



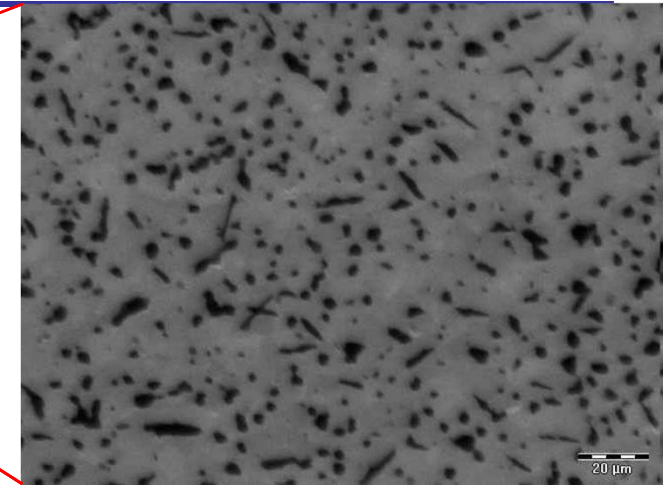
Ultra High Temperature Continuous Fiber Composites



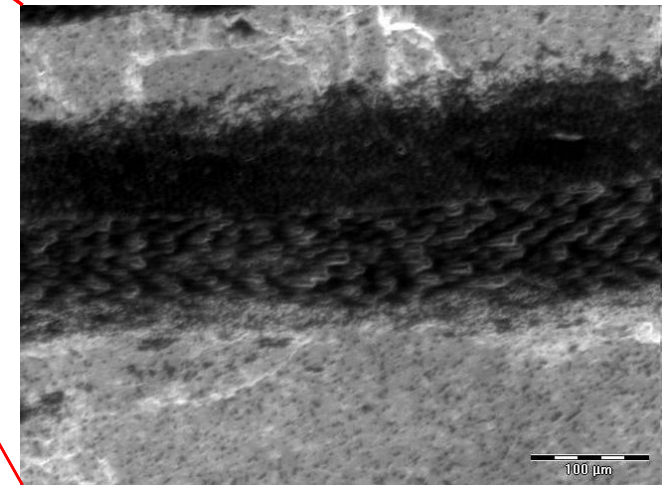
2D Composite microstructure



Monolithic microstructure



Dense UHTC matrix with acicular SiC.

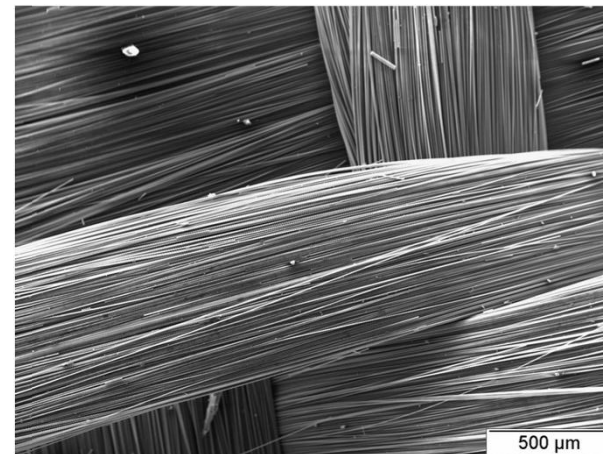


C fibers present after processing.¹⁵



Woven 3-D Carbon Fabric

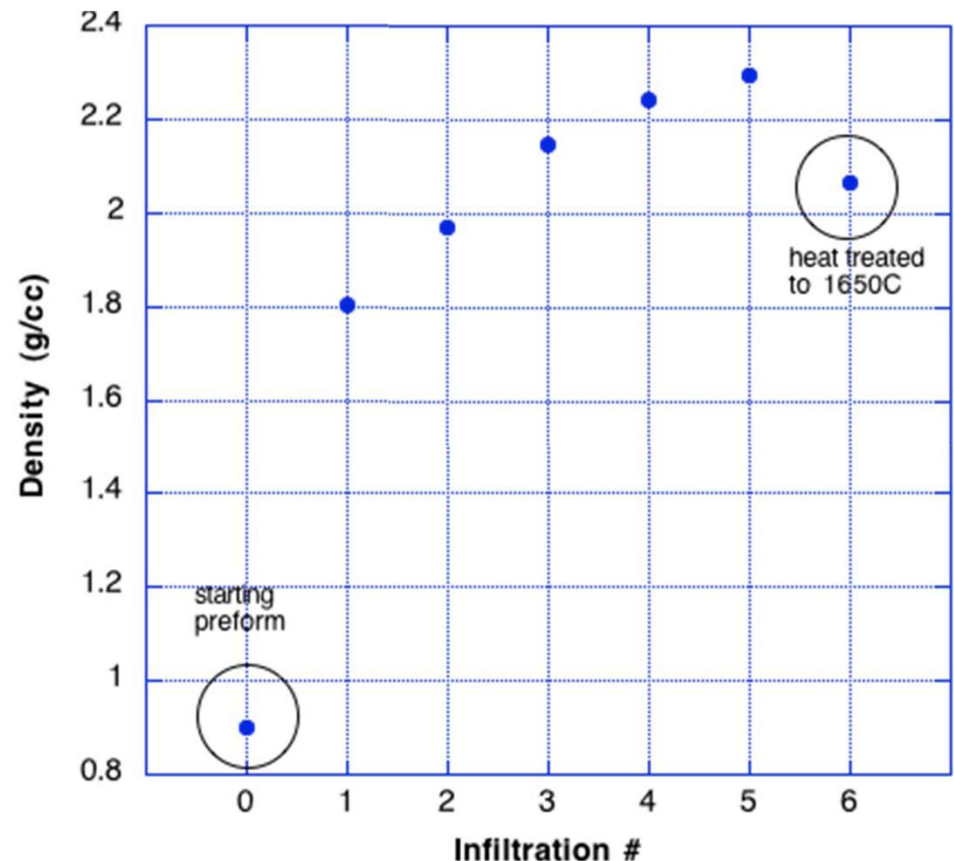
- 3D carbon preform
- PAN based fibers
- $V_f \sim 55\%$
- Density ~ 0.85 g/cc





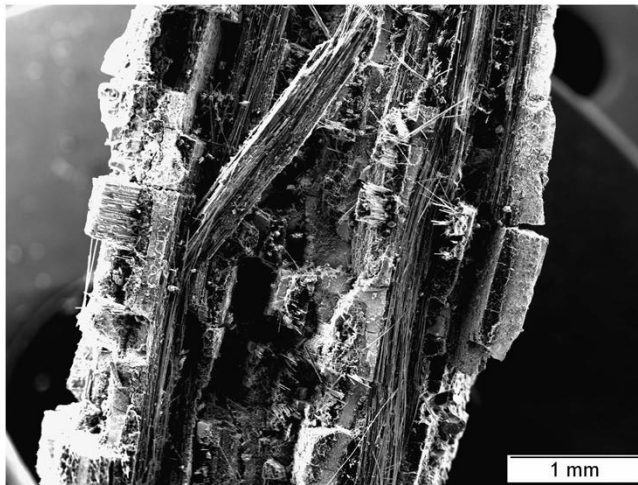
3D Woven Composite Infiltration

- Sample infiltrated with milled HfB_2 powder followed by repeated infiltrations with preceramic polymer
 - SiC precursor
- Sample heat treated to $> 600^\circ\text{C}$ between infiltrations to convert the polymer and remove organics
- Final heat treatment to 1650°C
- Initial density $\sim 0.9\text{g/cc}$
- Final density $\sim 2.1\text{g/cc}$

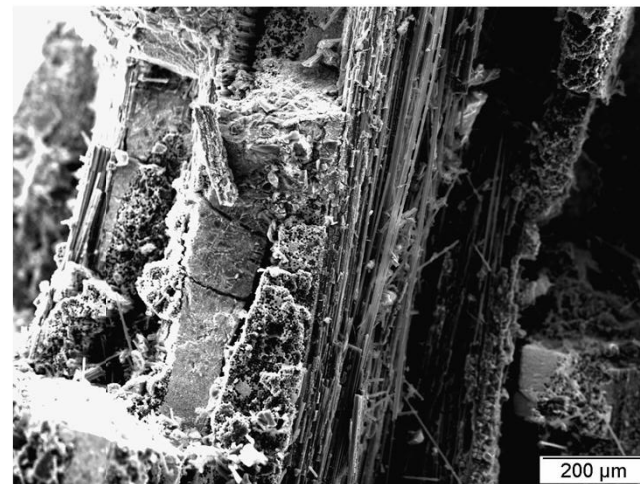
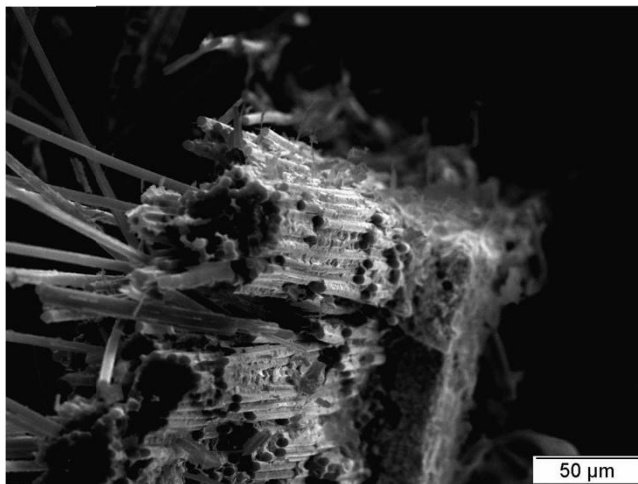




Fracture Surface of 3D Composite



- Non-uniform infiltration
- Accumulation on surface
- Infiltration throughout the thickness
- Infiltration into fiber bundles
- Brittle fracture

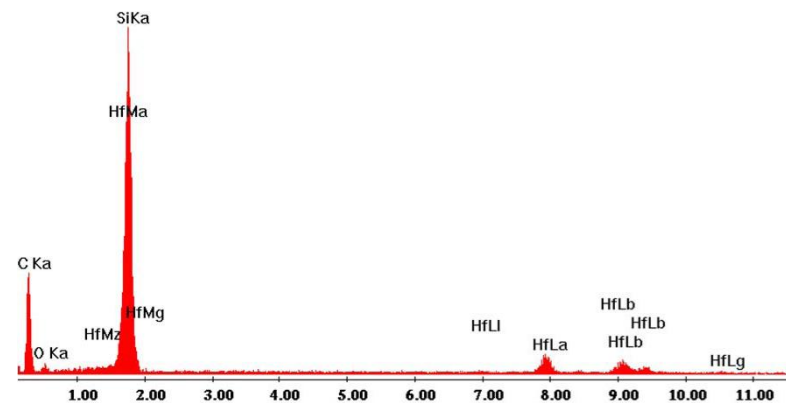
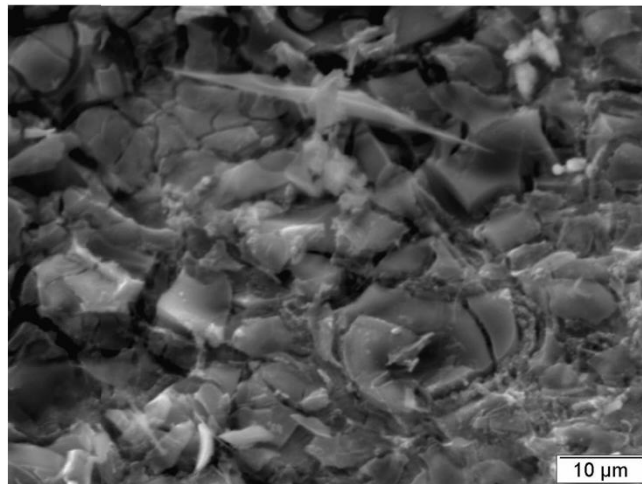


Infiltrated fiber bundle



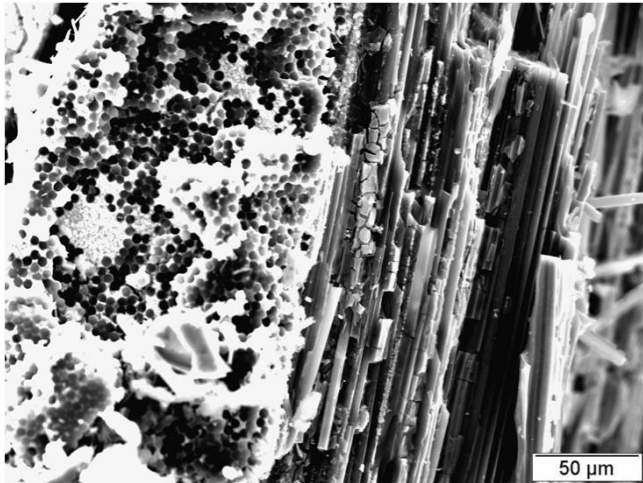
Polymer-Rich Matrix

- Matrix is generally a mix of HfB_2 powder and polymer
- Matrix infiltrates densely in some areas; poorly in others



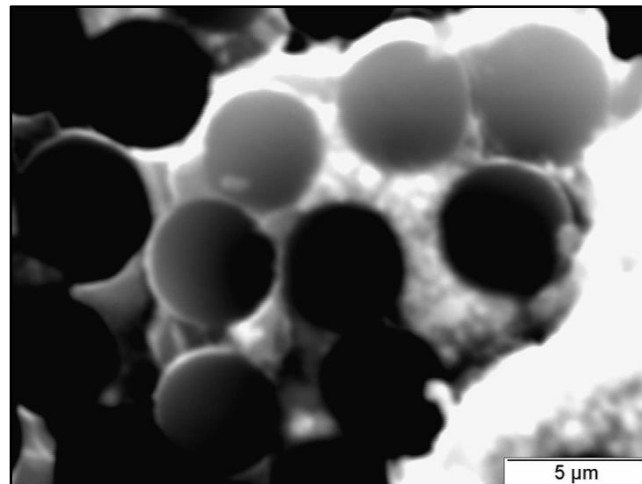
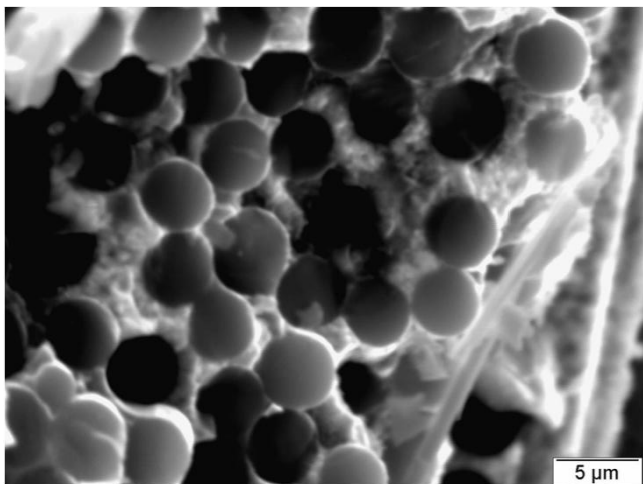


Infiltration of Powder and Polymer into Fiber Bundles



- Non-uniform
- Both polymer and powder infiltrate between fibers

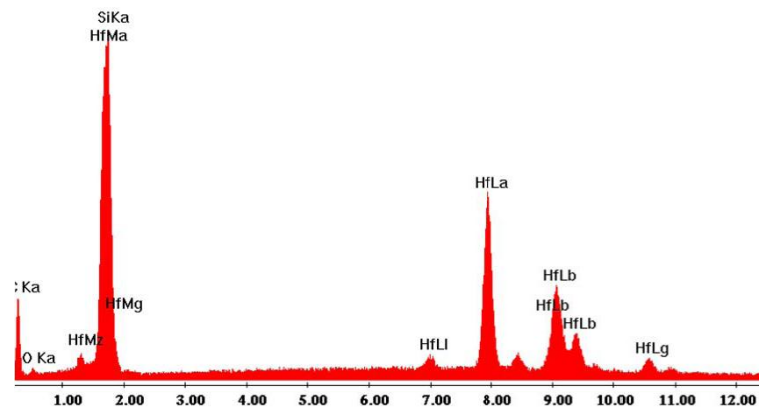
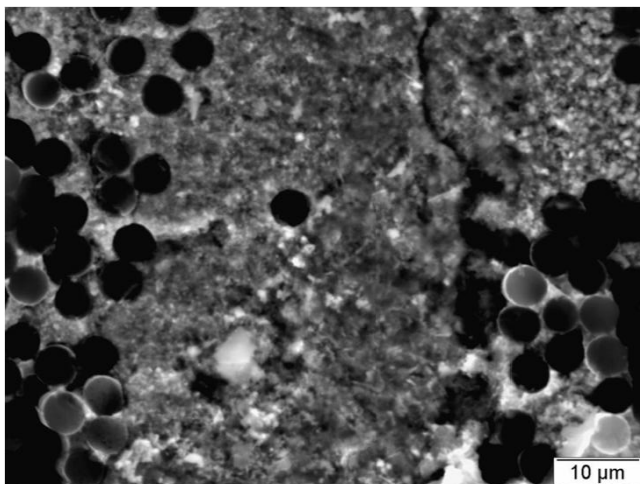
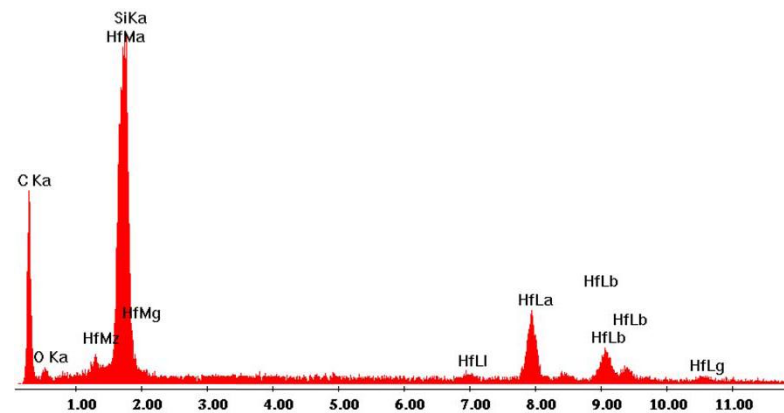
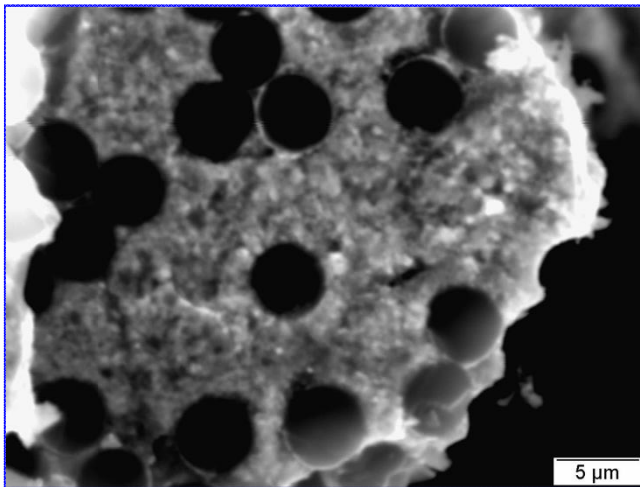
HfB₂ powder





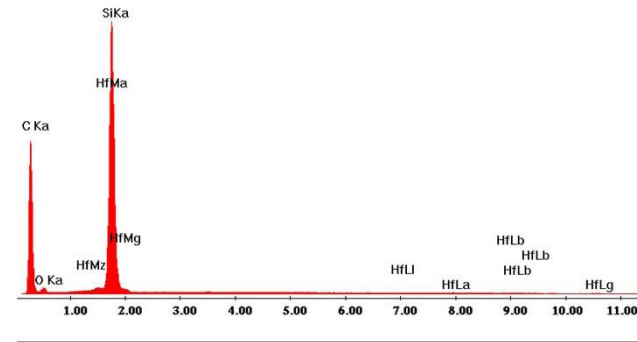
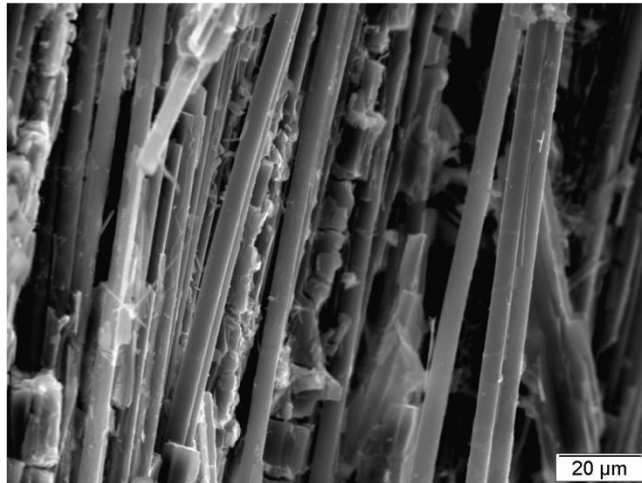
Infiltration of Fiber Bundles

Both powder and polymer infiltrate fiber bundles





Infiltration into 3D weave

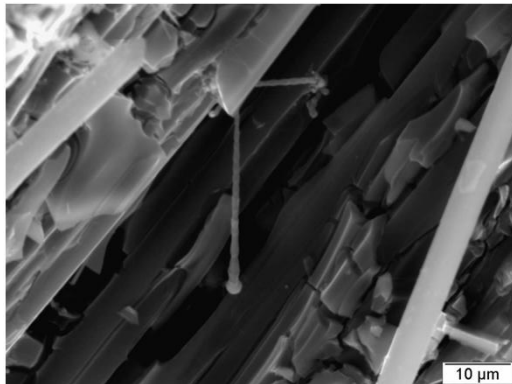
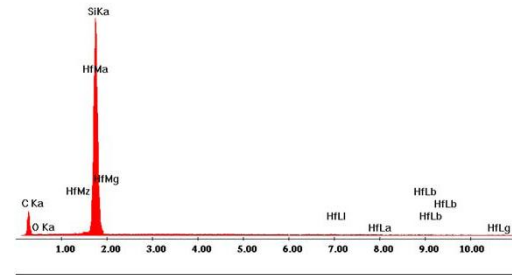
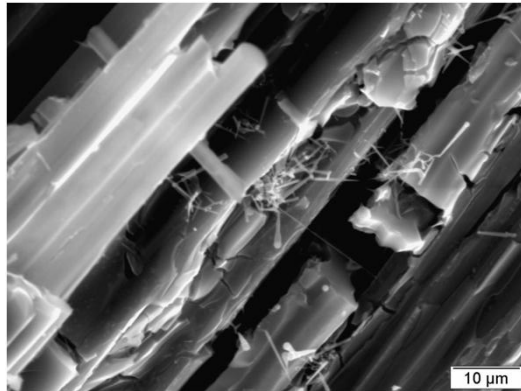


Preceramic polymer infiltrates throughout the sample

Powders infiltrate non-uniformly



Whiskers Growing on Fibers



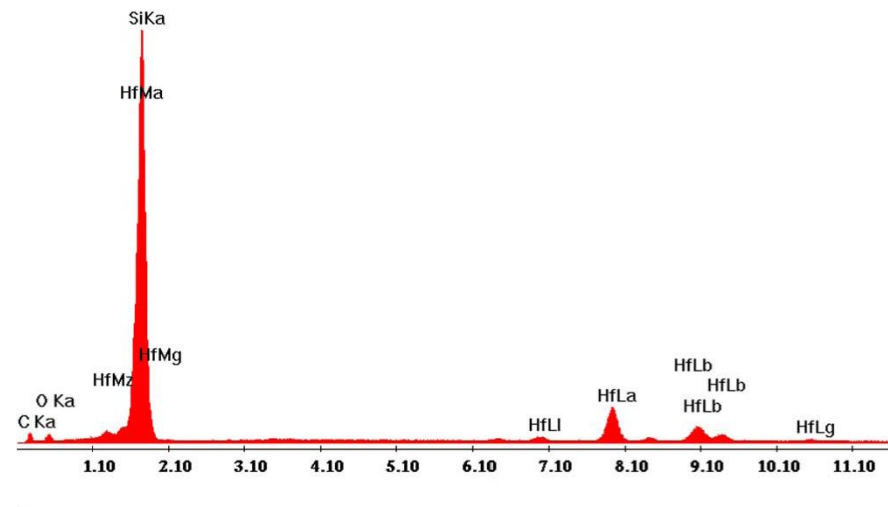
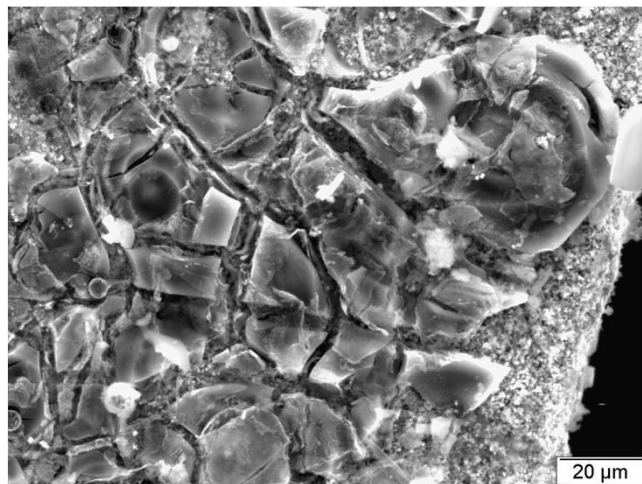
SiC whiskers grow in poorly-infiltrated areas.



Edge

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Label A: 3D Carbon With HfB2 SiC 800X Edge



Powder and polymer build up on edge of weave



Summary

- Have two approaches to *in-situ* reinforcement of HfB_2
 - Preceramic polymers
 - Fluidized bed process for “coating”
- Can infiltrate 2D C fiber weave and achieve desired matrix microstructure
- Can infiltrate 3D C fiber weave
 - Non-uniform infiltration
 - Powder and polymer both penetrate
 - Significant amount of infiltration
 - Growth of SiC whiskers in poorly-infiltrated areas
- Final microstructure unknown



Future Work

- Refine infiltration process
- Complete high temperature treatments of infiltrated composites
- Characterize microstructure